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TITLE: DECONVOLUTION ANALYSIS TO DETERMINE RELAXATION TIME SPECTRA OF INTERNAL FRICTION PEAKS

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DECONVOLUTION ANALYSIS TO DETERMINE RELAXATION TIME SPECTRA OF INTERNAL FRICTION PEAKS

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Résumé - On décrit une nouvelle méthode d'analyse des pics de frottement intérieur en fonction de la température. Elle permet d'obtenir une approximation du spectre des temps de relaxation responsables du pic. On montre que cette méthode, appelée analyse directe du spectre (DSA), s'applique à différents types de spectres: (i) elle fournit des approximations de certaines formes de spectre qui reproduisent la position, l'amplitude, la largeur et la forme avec une bonne précision, qui est de l'ordre de 10% (ii) elle ne conduit pas à des approximations aléatoires de la forme spectrale des pics.

Abstract - A new method for analysis of an internal friction vs temperature peak to obtain an approximation of the spectrum of relaxation times responsible for the peak is described. This method, referred to as direct spectrum analysis (DSA), is shown to provide an accurate estimate of the distribution of relaxation times. The method is validated for various spectra, and it is shown that: (i) It provides approximations to known input spectra which replicate the position, amplitude, width and shape with good accuracy (typically 10%). (ii) It does not yield approximations which have false spectral peaks.

I - Introduction

The problem of analyzing internal friction vs temperature peaks to determine the distribution of relaxation times responsible for the peak has been a difficult one for many years. The traditional method of analysis has been to assume various forms for the relaxation time spectrum and then choose the best form based upon goodness-of-fit to the data. The problem with this method is that none of the trial forms for the spectrum may be close to the true distribution. It would be preferrable to directly analyze the data to obtain an approximation of the spectrum, thus avoiding unnecessary assumptions. Such a method, referred to as direct spectrum analysis (DSA), has been developed and validated for approximating relaxation time spectra for processes with first-order kinetics /1/. With this method, nonlinear regression least-squares is used to unfold the integral equation for exponential decay with a distribution of relaxation times as the time constants within the integral. In a later paper /2/, the same method was applied to the Debye function as the kernel. This allowed analysis of internal friction (or dielectric relaxation) peaks when measured as a function of frequency. In the present paper these methods are extended to the measurement of internal friction vs temperature peaks.

II - Method

This method has some minimal requirements of the data. First, it is necessary that the internal friction vs temperature data have had background subtracted. It is important that this subtraction be done with the highest possible accuracy because the DSA method tends to find contributions to the relaxation time spectrum for any internal friction which may be present over and above that for a given peak. Second, it is necessary that there be roughly 20 or more data points; as has previously been shown /1,2/, the resolution capabilities of the method increase with both number and accuracy of the data points.

To discuss the method we will use the notation and development of Nowick and Berry /3/. We consider dynamic experiments in which stress is applied periodically at frequency ω so that for an anelastic solid there will be a phase lag of the strain behind the stress. The angle of this phase lag is φ, the loss angle, and the compliance is described by two dynamic response functions, a real part, J_1,

and an imaginary part, J_2. The internal friction is given by $\tan\varphi = J_2/J_1$. For a standard anelastic solid /3/ responding to periodic stress, these two dynamic response functions are given by

$$J_1 = J_u + \frac{\delta J}{1 + (\omega\tau)^2} \tag{1}$$

$$J_2 = \delta J \frac{\omega\tau}{1 + (\omega\tau)^2} \tag{2}$$

where $\delta J = J_r - J_u$, $\Delta = \delta J / J_u$ is the strength of the anelastic relaxation and J_r and J_u are the relaxed and the unrelaxed compliances, respectively.

Because the internal friction is measured as a function of temperature, certain corrections for temperature-dependent parameters are required. Nowick and Berry again provide an excellent discussion of these temperature corrections /3/. First, since we want our approximation of the relaxation time spectrum at some constant temperature, T_{disp}, we must correct ω and Δ to this temperature. For implementation of these two corrections, the reader is referred to Weller, et al /4/. Correction of Δ to T_{disp} involves a Curie-Weiss temperature dependence. Thus, it is required that a value be chosen for the critical temperature, T_c. Since the value may not be known, it is important to do the analysis using upper and lower limiting estimates of this parameter.

Analysis involves making two approximations both of which are valid for the usual experimental condition that $\tan\varphi << 1$. First, we consider $J_1 \simeq J_u$ so that $\tan\varphi \simeq J_2/J_u$. Second, we consider that the τ which is measured (the relaxation time at constant stress) is equal to the average τ (the one in the above equations) /3/. We now proceed to obtain our approximation of $N(\ln\tau)$, the spectrum of relaxation times at T_{disp}. We first specify the upper and lower τ limits for the spectrum. For the first attempt a wide range is chosen; with later tries this is adjusted keeping the range sufficient to show the tail regions of the spectrum. We next divide the range of $\log_{10}\tau$ into n bins of equal width and designate the relaxation time of the ith bin as τ_i, the midpoint value ($\log_{10}\tau$ scale) of the bin. The number of bins chosen depends upon the resolution desired. It is typically $10 \le n \le 100$, but with the constraint $n \le m$, where m is the number of data points.

The crux of the DSA method is to make a sum approximation for the integral (see Ref. 2) which contains the function $N(\ln\tau)$. This gives

$$\tan\varphi \simeq \frac{J_2}{J_u} \simeq \sum_{i=1}^{n} \Delta_i \frac{\omega\tau_i}{1 + (\omega\tau)^2}, \qquad \Delta = \sum_{i=1}^{n} \Delta_i \tag{3}$$

where Δ_i is the relaxation strength in the ith bin. Eq. (3) is the same as given by Nowick and Berry /3/ for multiple relaxations with discrete relaxation times. Thus, using this equation is the same as considering the relaxation to be made up of n different discrete relaxations all of which are equally spaced in $\log\tau$.

The τ_i in Eq. 3 will exhibit a temperature dependence according to the Arrhenius relation, $\tau = \tau_0 \exp(Q/kT)$, where τ_0 is the pre-exponential factor, Q is the activation energy and k is Boltzmann's constant. For a given measurement of the internal friction at some temperature other than T_{disp}, the τ_i need to be corrected to their values at T_{disp}. This is done using either of two models for the distribution of relaxation times as discussed by Nowick and Berry /3/. The first model considers that the distribution is only due to a distribution of activation energies and that τ_0 is constant. The second model is just the opposite of the first, i.e., there is only distribution of τ_0's and Q is a constant. We will use the first of these models in the discussion which follows, although the second has been used and found to provide good spectral estimates.

After choosing n and the τ limits for the spectrum, we continue as follows: (i) Choose T_{disp}; typically this will be the temperature of the peak. (ii) Input the experimental value for ω. (iii) Provide an estimate of τ_0. (iv) Estimate the total relaxation strength, Δ. Typically, this is estimated as twice the peak height, Q^{-1}_{max}. To start the iteration process we set the Δ_i, the relaxation strength in the ith bin, all to the same value, $\Delta_i = \Delta/n$. The nonlinear regression least-squares method is now ready to be used. It will iterate adjusting the Δ_i to minimize the least-square differences between the calculated and the experimental points. We terminate the calculation by either choosing a desired number of iterations or by a statistical evaluation of convergence.

III. - VALIDATION

The validation method is one of generating an artificial set of internal friction data from a known relaxation time spectrum, adding random (Gaussian) error with a desired standard deviation, and then applying the DSA method to the data to test how well the input spectrum is recovered. In the examples which follow, the input distribution of relaxation times was either a single lognormal or a

combination of several lognormal (Gaussian in $\log_{10}\tau$) distributions.

Fig. 1 shows an example of such a computer-generated internal friction peak plotted vs reciprocal temperature. The internal friction is normalized as tan φ/Δ. The data at the various temperatures have been calculated from the Arrhenius relation with an activation energy, Q=1.4 eV and pre-exponential, $\tau_0=10^{-14}$ s. The 50 data points have been generated for $\omega=1.0$ s from a single lognormal distribution centered at $\tau_m=1.0$ s and with width $\beta=1.0$. Random fractional error with standard deviation $\sigma=0.01$ has been added to the data.

Fig. 2 shows the histogram for the start of the nonlinear regression analysis of the data in Fig. 1. Each of the 40 bins has equal spectral amplitude such that the area of the histogram is unity (on a ln τ scale). The spectral limits for the calculation have been chosen to cover three decades with the center at roughly $\tau=1/\omega$. Fig. 3 shows on the same axes the histogram approximation of the input spectrum for $T_{dist}=500$ K after 500 iterations using DSA and assuming τ_0 to be 10^{-14} s. At the top of the figure the scale is for the equivalent activation energy. It may be noted that the histogram approximation agrees well with the original input distribution which is shown as a solid curve in the figure. A lognormal fit to the histogram gives $\tau_m=1.02$ s and $\beta=1.03$ in good agreement with these parameters for the input spectrum.

Validation was also done for input spectra with a single lognormal distribution, but for values of β ranging from 0.25 to 3.0 and random fractional error with $\sigma=0.01$. As with the result in Fig. 3, the DSA method was found to provide a good approximation of the input spectra over this range of β. The capability of the method to give good spectral approximations for symmetrical distributions with widths ranging from that of a nearly discrete relaxation ($\beta=0.25$) to distributions covering up to five decades in τ is encouraging.

To examine the recovery of asymmetrical spectra, data were generated from multiple, but overlapping, lognormal spectra of varying widths. These spectra gave overlapping internal friction peaks which would be expected to be very difficult to deconvolute. An example of such a complex peak is shown in Fig. 4 as a broad internal friction peak made up as the sum of four separate peaks shown as dashed curves. Again, 50 data points have been used for $\omega=1.0$. Fractional error with standard deviation $\sigma=0.01$ has been added to simulate experiment. The four separate peaks are each generated from a lognormal distribution. These vary in fractional strength and width and are centered roughly a factor of four apart as shown in Fig. 5.

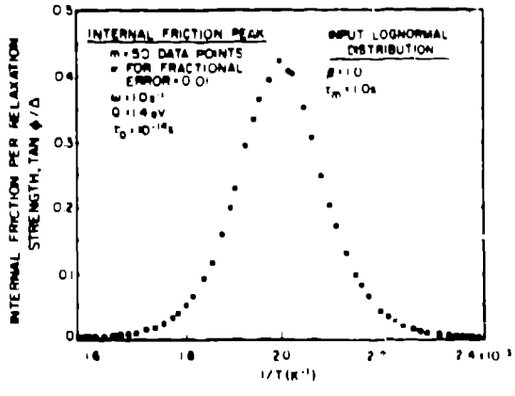

Fig. 1 - Internal friction vs temperature data generated from a lognormal distribution to check the capability of the DSA method to recover the input spectrum.

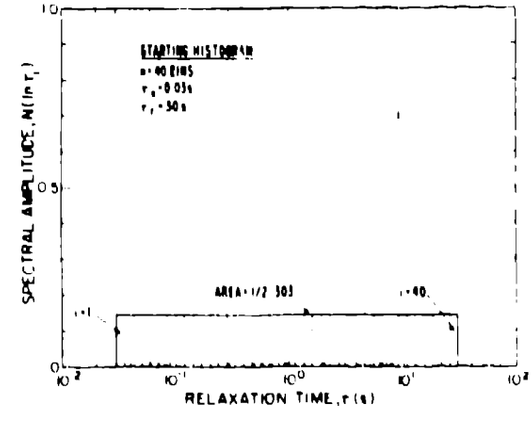

Fig. 2 - Starting histogram for calculation of the DSA approximation to the input spectrum. The vertical dashed lines are the spectral limits.

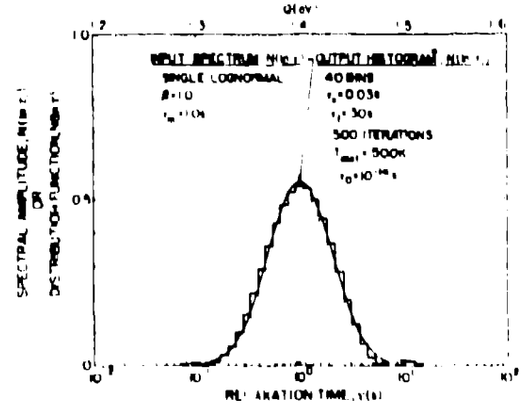

Fig. 3 - Input relaxation time spectrum and output histogram approximation after DSA of data in Fig. 1.

The results of the calculation using the DSA method on the data in Fig. 4 are also shown in Fig. 5. Here they may be compared with the input spectrum (solid curve) which defines the internal friction peak. The histogram approximation of the input spectrum is done at T_{dist}=500 K for 40 bins of τ. The only assumption used for the calculation was that $\tau_0=10^{-14}$ s. It may be seen that the DSA approximation shows very satisfactory agreement with the spectrum which was used to generate the data. It is particularly satisfying that the analysis is able to reproduce the four peaks which make up the input spectrum. Similar validations using input spectra of two and three peaks also showed this good resolving power. Many different kinds of spectra have been validated using the method described here. Importantly, these validations never gave false approximations to the input spectrum, i.e., in no case did the results of the DSA show extra peaks or miss peaks which were of reasonable magnitude (~10% of the total spectrum).

The validation described in Fig. 5 demonstrates that the amplitude, shape, width and location of the peaks are all reconstructed with acceptable accuracy. Only a minor difficulty is evident; this is for the location of the third peak. The histogram shows this peak to be at a relaxation time which is roughly 40% too high. This tendency was observed in other analyses, particularly when the input peaks were close together. Typically, the method resolves input peaks which are a factor of two or more apart, but the peaks tend to be displaced away from each other as shown in Fig. 5.

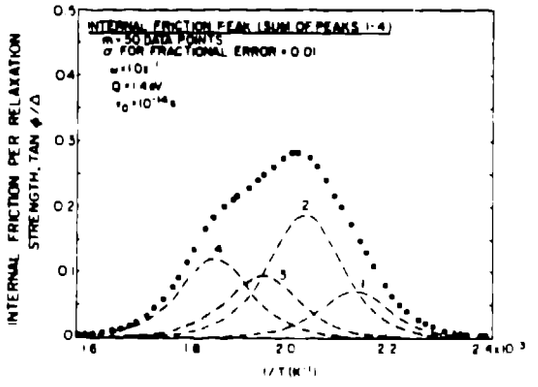

Fig. 4 - Internal friction data generated from 4-peak input spectrum.

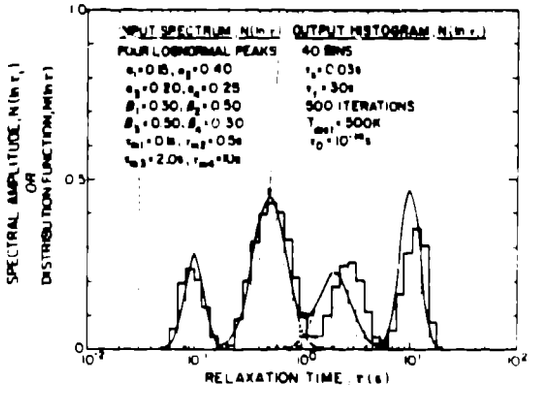

Fig. 5 - Input relaxation time spectrum and output histogram approximation after DSA of the data in Fig. 4. The α's are the fractional contribution of each lognormal spectrum.

V - CONCLUSIONS

(a) A new method is described for analysis of an internal friction vs temperature peak to obtain an approximation of the spectrum of relaxation times responsible for the peak.

(b) It is shown that this method provides approximations to known input spectra which replicate the position, amplitude, width and shape with good accuracy (typically ~10%).

(c) Validation of this method for a wide variety of spectra shows that it does not yield approximations which have false spectral peaks.

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